

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-105792

(43)Date of publication of application : 08.04.2004

(51)Int.Cl. B01J 23/58  
B01D 53/94  
B01J 35/04

(21)Application number : 2002-268245

(71)Applicant : TOYOTA MOTOR CORP

(22)Date of filing : 13.09.2002

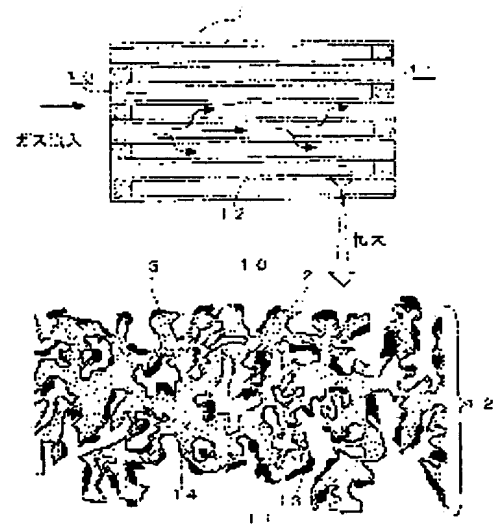
(72)Inventor : OGAWARA SEIJI

## (54) CATALYST FOR EXHAUST GAS PURIFICATION FILTER AND METHOD OF MANUFACTURING THE SAME

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To further improve PM (Particulate Matter) removing capability, pressure loss detection sensitivity, and durability of NOx removing capability.

**SOLUTION:** A catalytic layer containing a first carrier 2 with an average particle diameter of  $\leq 1 \mu\text{m}$ , a 2nd carrier 3 with an average particle diameter in the range of 1/20 to 1/2 of the average pore diameter of the cell partition and a catalytic metal is formed on the surface of a cell partition 12 having fine pores with the average pore diameter of 20 to 40  $\mu\text{m}$  and on the inner surface of the fine pores. The catalytic layer has parts where the second carrier 3 exists and does not exit, and its surface is uneven. The 2nd carrier 3 does not easily enter the fine pores with the diameter of  $\leq 20 \mu\text{m}$ , and is unevenly distributed on the cell partition surface or in fine pores with a large diameter. As a result, the PM collides with raised sections and is easily caught, which increases the chances of contact with the catalytic metal.



## LEGAL STATUS

[Date of request for examination] 20.04.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

\* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1]

the cel septum which divides the inflow side cel by which the weather strip was carried out by the exhaust gas downstream, the outflow side cel by which adjoined this inflow side cel and the weather strip was carried out by the exhaust gas upstream, and this inflow side cel and this outflow side cel, and has the pore whose average pore size is 20-40 micrometers -- since -- the becoming honeycomb structure object, the catalyst bed which is formed in the front face and pore internal surface of this cel septum, and contains the 1st support whose mean particle diameter is a porosity oxide 1 micrometer or less, the 2nd support which is the porosity oxide which has mean particle diameter in the range of  $1/20 - 1/2$  of the average pore size of this cel septum, and a catalyst metal -- since  
The emission-gas-purification filter catalyst characterized by for there being a part in which this 2nd support exists, and a part not existing in this catalyst bed, and the front face of this catalyst bed having become tooth-like.

[Claim 2]

Said 2nd support is an emission-gas-purification filter catalyst according to claim 1 currently supported by the front face of the layer which consists of said 1st support.

[Claim 3]

The emission-gas-purification filter catalyst according to claim 1 whose porosity of said cel septum is 60 - 80%.

[Claim 4]

Said catalyst bed is NO<sub>x</sub> chosen from the alkali metal, alkaline earth metal, and rare earth elements which were supported by either [ at least ] said 1st support or said 2nd support. Emission-gas-purification filter catalyst containing occlusion material according to claim 1 to 3.

[Claim 5]

Said catalyst bed is NO<sub>x</sub> at low temperature. It adsorbs and is NO<sub>x</sub> at an elevated temperature. NO<sub>x</sub> to emit  
Emission-gas-purification filter catalyst containing adsorption material according to claim 1 to 3.

[Claim 6]

the cel septum which divides the inflow side cel by which the weather strip was carried out by the exhaust gas downstream, the outflow side cel by which adjoined this inflow side cel and the weather strip was carried out by the exhaust gas upstream, and this inflow side cel and this outflow side cel, and has the pore whose average pore size is 20-40 micrometers -- since -- the becoming honeycomb structure object -- preparing

The manufacture approach of the emission-gas-purification filter catalyst which carries out the wash coat of the slurry to which mean particle diameter is mainly concerned with a porosity oxide 1 micrometer or less to this cel septum, and is characterized by forming the 1st support layer, carrying out the wash coat of the slurry which is mainly concerned with the porosity oxide which has mean particle diameter subsequently to the range of  $1/20 - 1/2$  of the average pore size of this cel septum to this cel septum, and forming the 2nd support layer.

---

[Translation done.]

**\* NOTICES \***

**JPO and NCIPi are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the emission-gas-purification filter catalyst which purifies the exhaust gas containing a particulate, such as exhaust gas from a diesel power plant, and its manufacture approach.

[0002]

[Description of the Prior Art]

About the gasoline engine, the injurious ingredient in exhaust gas has been decreasing certainly by severe regulation of exhaust gas, and advance of the technique in which it can be coped with. However, about the diesel power plant, the advance of a technique is also behind also in regulation from the unique situation that an injurious ingredient is discharged as a particulate (particulate matter: sulfur system particles, such as a carbon particle and sulfate, the amount hydrocarbon particle of macromolecules, etc. are called following PM), compared with the gasoline engine.

[0003]

As an exhaust gas purge for diesel power plants currently developed by current, it roughly divides and the exhaust gas purge (Wall flow) of a trap mold and the exhaust gas purge (straight flow) of an open type are known. Among these, as an exhaust gas purge of a trap mold, the \*\*\*\*\* type honeycomb object made from a ceramic (diesel PM filter (it is called Following DPF)) is known. Discharge controls by this DPF consisting of a cel septum which divides the inflow side cel by which comes to \*\*\*\*\* the both ends of opening of the cel of a ceramic honeycomb structure object in checkers by turns, and the weather strip was carried out by the exhaust gas downstream, the outflow side cel by which adjoined the inflow side cel and the weather strip was carried out by the exhaust-gas upstream, and an inflow side cel and an outflow side cel, filtering exhaust gas by the pore of a cel septum, and carrying out uptake of the PM.

[0004]

However, since a pressure loss goes up by deposition of PM, it is necessary to remove periodically PM deposited with a certain means, and to reproduce in DPF. Then, when a pressure loss goes up conventionally, reproducing DPF by burning PM deposited in the burner or the electric heater is performed. However, in this case, the temperature at the time of combustion rises, so that there is much alimentation of PM, and DPF may be damaged with the thermal stress by it.

[0005]

So, in recent years, a coat layer is formed in the front face of the cel septum of DPF from an alumina etc., and the continuation playback type DPF which supported catalyst metals, such as platinum (Pt), in the coat layer is developed. Since PM by which uptake was carried out carries out oxidation combustion by the catalytic reaction of a catalyst metal according to this continuation playback type DPF, DPF is reproducible by making it burn simultaneous in uptake succeeding uptake. And since catalytic reaction can burn while there are few being comparatively generated at low temperature and amounts of uptake, it has the advantage that the thermal stress which acts on DPF is small, and breakage is prevented.

[0006]

As such a continuation playback type DPF, the porosity coat layer which consists of an activated alumina of a bigger particle size than the average pore size of a cel septum is formed in the front face of a cel septum, the interior of pore is coated with the activated alumina of a particle size smaller than the average pore size of a cel septum, and what supported the catalyst metal further is indicated by JP,09-173866,A. According to this continuation playback type DPF, a pressure loss can be made low, making the specific surface area of a coat layer increase.

[0007]

Moreover, the thing of a configuration of that, as for the porosity oxide with which average pore size is 5-35 micrometers, and the porosity of a cel septum constitutes a coat layer from 40 - 65%, the thing of a particle size smaller than the average pore size of a cel septum occupies more than 90wt% is indicated by JP,09-220423,A. A coat layer can be formed even in the inner surface of not only the front face of a cel septum but pore by carrying out the coat of such a porosity oxide of high specific surface area. Moreover, since fixed, then coat thickness can be made thin for the amount of coats, increase of a pressure loss can be controlled.

[0008]

And in JP,06-159037,A, it is NO<sub>x</sub> further to the above-mentioned coat layer. The continuation playback type DPF which supported occlusion material is indicated. It will be NO<sub>x</sub> if it does in this way. It is NO<sub>x</sub> to occlusion material. NO<sub>x</sub> by which occlusion was carried out by being able to carry out occlusion and spraying reducing agents, such as gas oil, It becomes possible to return and purify.

[0009]

However, in the continuation playback type DPF, the amount of coats is restrained from balance with a pressure loss, the amount of support of a catalyst metal cannot be made [ many ], but there is a problem that activity has constraint. It is because the support consistency of a catalyst metal will become large and endurance will fall with the grain growth at the time of an elevated temperature, if many catalyst metals are supported in a thin coat layer.

[0010]

For example, with the technique given in JP,09-173866,A, a slurry is prepared from the mixed powder of the alumina powder of a big particle size, and the alumina powder of a small particle size, and the coat layer is formed by carrying out a wash coat to DPF. However, by this approach, the big particle which invades in pore also exists not a little, and has a possibility that pore may be blockaded and a pressure loss may increase with a small particle. Moreover, if the amount of coats is lessened in order to prevent increase of a pressure loss, the support consistency of a catalyst metal will become large and endurance will fall with the grain growth at the time of an elevated temperature.

[0011]

Furthermore, it is NO<sub>x</sub> to a coat layer. It is NO<sub>x</sub> if there are few amounts of coats by the continuation playback formula DPF containing occlusion material. Reactions, such as dissolution, arise between occlusion material and filter base material, and it is NO<sub>x</sub>. There is a problem that decontamination capacity falls. Then, if the amount of coats is made [ many ], although the reaction with filter base material will be controlled, they are exhaust gas and NO<sub>x</sub> by lock out of pore. A contact probability with occlusion material falls and it is NO<sub>x</sub>. Decontamination capacity falls. Moreover, a pressure loss will also go up and PM collection efficiency will also fall.

[0012]

By the way, in the situation that uptake of the PM is carried out into the pore of a cel septum, since the contact probability of PM and a catalyst metal is high and heat retaining property is high, oxidation reaction of PM advances smoothly. Moreover, since a pressure loss increases sensitively in connection with the uptake of PM, the alimentation of PM can be presumed by detecting a pressure loss. Therefore, it can prevent that can burn PM in the alimentation within a basis and the continuation playback type DPF serves as an elevated temperature at the time of combustion by regenerating passing hot exhaust gas etc. when a pressure loss exceeds a reference value.

[0013]

[Patent reference 1] JP,09-173866,A

[0014]

[Patent reference 2] JP,09-220423,A

[0015]

[Patent reference 3] JP,06-159037,A

[0016]

[Problem(s) to be Solved by the Invention]

However, when the conditions by which the time of low temperature and PM are discharged so much continue, the rate of sedimentation becomes large from the oxidation rate of PM, and PM is deposited in the shape of a layer along with a cel septum. In order that PM deposited on the front face of a cel septum in the shape of a layer may oxidize only by the interface with a cel septum on condition that usual, between a deposit and a cel septum, an opening is generated, the fall degree of the pressure loss accompanying the increment in alimentation becomes small, and pressure-loss detection sensitivity falls. Therefore, by the

approach of detecting a pressure loss and presuming PM alimentation, there is fault that the difference of presumed PM alimentation and actual alimentation is large.

[0017]

Moreover, once an opening is generated between a deposit and a cel septum, in order not to contact a catalyst metal, the oxidation rate of PM will fall, surface deposition will advance further, and alimentation of the front face of a deposit will increase extremely. Therefore, PM deposited when exhaust gas temperature rose burns at a stretch, and there is a problem that the continuation playback type DPF serves as an elevated temperature, and a catalyst metal carries out grain growth, and deteriorate, or an erosion arises.

[0018]

While this invention is made in view of such a situation and raises PM decontamination capacity, it aims at controlling the fall of pressure-loss detection sensitivity.

[0019]

[Means for Solving the Problem]

the cel septum which the description of the emission-gas-purification filter catalyst of this invention which solves the above-mentioned technical problem divides the inflow side cel by which the weather strip was carried out by the exhaust gas downstream, the outflow side cel by which adjoined the inflow side cel and the weather strip was carried out by the exhaust gas upstream, and an inflow side cel and an outflow side cel, and has the pore whose average pore size is 20-40 micrometers -- since -- the becoming honeycomb structure object,

the catalyst bed which is formed in the front face and the pore internal surface of a cel septum, and contains the 1st support whose mean particle diameter is a porosity oxide 1 micrometer or less, the 2nd support which is the porosity oxide which has mean particle diameter in the range of  $1/20 - 1/2$  of the average pore size of a cel septum, and a catalyst metal -- since -- there are a part in which the 2nd support exists, and a part not existing in a catalyst bed, and it is in the front face of a catalyst bed having become tooth-like.

[0020]

The 2nd support has especially the desirable thing currently supported by the front face of the layer which consists of the 1st support. Moreover, it is still more desirable for the porosity of a cel septum to be 60 - 80%.

[0021]

A catalyst bed is NO<sub>x</sub> chosen from the alkali metal, alkaline earth metal, and rare earth elements which were supported by either [ at least ] the 1st support or the 2nd support. It is NO<sub>x</sub> at occlusion material or low temperature. It adsorbs and is NO<sub>x</sub> at an elevated temperature. NO<sub>x</sub> to emit It is desirable to include adsorption material.

[0022]

And the description of the manufacture approach of the emission-gas-purification filter catalyst of this invention The inflow side cel by which the weather strip was carried out by the exhaust gas downstream, and the outflow side cel by which adjoined the inflow side cel and the weather strip was carried out by the exhaust gas upstream, The cel septum which divides an inflow side cel and an outflow side cel, and has the pore whose average pore size is 20-40 micrometers, Prepare the becoming honeycomb structure object, carry out the wash coat of the slurry to which mean particle diameter is mainly concerned with a porosity oxide 1 micrometer or less to a cel septum, and the 1st support layer is formed. since -- Subsequently, it is in mean particle diameter carrying out the wash coat of the slurry which is mainly concerned with the porosity oxide in the range of  $1/20 - 1/2$  of the average pore size of a cel septum to a cel septum, and forming the 2nd support layer.

[0023]

[Embodiment of the Invention]

With the emission-gas-purification filter catalyst of this invention, the catalyst bed which contains in the cel septum the 1st support whose mean particle diameter is a porosity oxide 1 micrometer or less, the 2nd support which is the porosity oxide which has mean particle diameter in the range of  $1/20 - 1/2$  of the average pore size of a cel septum, and a catalyst metal is formed using a honeycomb structure object with the cel septum which has the pore whose average pore size is 20-40 micrometers. Since mean particle diameter is 1 micrometer or less and is very detailed compared with the average pore size (20-40 micrometers) of a cel septum, the 1st support enters easily in the pore of a cel septum at the time of a wash coat, and forms a coat layer with thin thickness in a pore internal surface. Therefore, since decline in increase of a pressure loss and the collection efficiency of PM can be controlled and the contact probability of a catalyst metal and PM increases by regulating the amount of coats, PM decontamination capacity

improves. Moreover, since the contact probability of a harmful gas component and a catalyst metal also increases, they are HC, CO, and NOx. The rate of purification also improves.

[0024]

On the other hand, the 2nd support has mean particle diameter larger than the 1st support, is in the range of  $1/20 - 1/2$  of the average pore size of a cel septum, and is 1-20 micrometers and a comparatively big particle size. Therefore, pore size cannot enter easily in pore 20 micrometers or less at the time of a wash coat, and the 2nd support comes to be unevenly distributed in a cel septum front face or pore with big pore size. Therefore, in the part in which the 2nd support does not exist, it is thin meat and becomes a heavy-gage tooth-like catalyst bed in the part in which the 2nd support exists. Since uptake becomes easy to be carried out in order that PM may collide with a part for heights by this, and a contact probability with a catalyst metal increases, PM uptake ability and PM decontamination capacity improve. It comes to increase sensitively, without furthermore saturating a pressure loss with the increment in the amount of uptake of PM, and the fall of pressure-loss detection sensitivity is controlled.

[0025]

Moreover, by the 2nd support, to a catalyst bed, a part with thick thickness is made partially, and the support consistency of a catalyst component becomes low in the part at it. Therefore, NOx It is NOx in a part with a catalyst bed thick when occlusion material is supported. The reaction of occlusion material and a cel septum can be controlled, when a support consistency is uniform, it compares, and it is NOx. The endurance of decontamination capacity improves.

[0026]

In addition, the average pore size of a cel septum is computable by carrying out the image processing of the microphotography of a cross section.

[0027]

A honeycomb structure object consists of a cel septum which divides the inflow side cel by which the weather strip was carried out by the exhaust gas downstream, the outflow side cel by which adjoined the inflow side cel and the weather strip was carried out by the exhaust gas upstream, and an inflow side cel and an outflow side cel.

[0028]

This honeycomb structure object can be manufactured from heat-resistant ceramics, such as cordierite. For example, the slurry of the shape of clay which uses cordierite powder as a principal component is prepared, and it is fabricated and calcinated by extrusion molding etc. It can replace with cordierite powder, and each powder of an alumina, a magnesia, and a silica can also be blended so that it may become a cordierite presentation. Then, cel opening of an end side is \*\*\*\*\* (ed) in the shape of a check etc. by the slurry of the shape of same clay etc., and cel opening of the cel which adjoins a \*\*\*\* suggestion \*\*\*\* cel in respect of an end in respect of the other end is \*\*\*\*\* (ed). A honeycomb structure object can be manufactured by fixing \*\*\*\*\* material by baking etc. after that.

[0029]

And in order for average pore size to form in the cel septum of a honeycomb structure object the pore which is 20-40 micrometers, combustible powder, such as carbon powder, wood flour, starch, and resin powder, etc. is mixed in the above-mentioned slurry, pore can be formed because combustible powder disappears at the time of baking, and the particle size and the porosity of pore can be controlled by adjusting the particle size and the addition of combustible powder. The cel of an entrance side and the cel of an outlet side are mutually open for free passage with this pore, and although uptake of the PM is carried out into pore, a gas can pass pore from an entrance-side cel to an outlet side cel. In addition, since the small pore of pore size carries out [ the average pore size of a cel septum ] blinding by the 1st support by less than 20 micrometers and a pressure loss increases, it is not desirable. Moreover, when average pore size exceeds 40 micrometers, there is a case where the reinforcement of a honeycomb structure object falls and it stops being equal to practical use.

[0030]

As for the porosity of a cel septum, it is desirable that it is 60 - 80%. By porosity being in this range, it is a catalyst bed. Even if it carries out 100- 200 g/L formation, increase of a pressure loss can be controlled, and a strong fall can also be controlled further. And uptake of the PM can be carried out still more efficiently.

[0031]

The catalyst bed which consists of the 1st support, the 2nd support, and a catalyst metal is formed in the front face and pore internal surface of a cel septum. The 1st support and the 2nd support can use the multiple oxide which consists of oxides, such as aluminum 2O3 from a porosity oxide, and ZrO2, CeO2, TiO2, SiO2,

or two or more of these sorts. It is good also as the same quality of the material, and the 1st support and the 2nd support can also be made into the different quality of the material. moreover, the percentage of the 1st support in a catalyst bed, and the 2nd support -- a weight ratio -- 1st support: -- the 2nd -- it is desirable to consider as the range of support =5:1-1:5. If there is more 1st support than this range, the small pore of a cell wall will carry out blinding, a pressure loss may increase, and if there is less 2nd support than this range, the effectiveness made into the shape of toothing will hardly be acquired. On the other hand, if there is less 1st support than this range, the contact probability of PM and a catalyst metal will fall and PM decontamination capacity will fall.

[0032]

What is necessary is to make oxide powder or multiple oxide powder into a slurry with a binder component and water, such as alumina sol, and just to calcinate, after making the slurry adhere to a cell septum in order to form a catalyst bed. Although dip coating usual to making a slurry adhere to a cell septum can be used, while filling up the pore of a cell septum with a slurry compulsorily by the air blow or suction, it is desirable to remove the extraneous article of a slurry which entered in pore.

[0033]

The mean particle diameter of the 1st support is a thing 1 micrometer or less, and the 2nd support has mean particle diameter in the range of  $1/20$  -  $1/2$  of the average pore size of a cell septum. Since the average pore size of a cell septum is 20-40 micrometers when the slurry containing the mixed powder of the 1st support and the 2nd support is prepared and a catalyst bed is formed by the wash coat method, the 1st support tends to go also into pore 20 micrometers or less, and adheres to the front face and pore internal surface of a cell septum at homogeneity. Since one 2nd support has a large particle size, it cannot go into pore 20 micrometers or less easily, is unevenly distributed in a cell septum front face and a pore internal surface with big pore size, and adheres. Therefore, in the part in which the 2nd support does not exist, it is thin meat and the catalyst bed of the shape of heavy-gage toothing is formed in the part in which the 2nd support exists.

[0034]

The amount of formation of the catalyst bed in this case is per [ honeycomb structure object 1L ]. It is desirable to be referred to as 100-200g. catalyst bed less than 100 g/L -- NOx the time of supporting occlusion material -- NOx the fall of the endurance of occlusion ability is not avoided -- a pressure loss becomes high too much and is not practical if 200 g/L is exceeded.

[0035]

By the manufacture approach of this invention done so still more effectively, the wash coat of the slurry to which mean particle diameter is mainly concerned with the 1st support 1 micrometer or less is carried out to a cell septum, and the above-mentioned operation forms the 1st support layer, carries out the wash coat of the slurry which is mainly concerned with the 2nd support which has mean particle diameter subsequently to the range of  $1/20$  -  $1/2$  of the average pore size of a cell septum to a cell septum, and forms the 2nd support layer. At the time of formation of the 1st support layer, the 1st detailed support adheres to the front face and almost all the pore internal surface of a cell septum at homogeneity. And since the aperture has become still smaller as for the pore in which it is hard to go into pore 20 micrometers or less since the 2nd support has a large particle size, and the 1st support layer is already formed at the time of formation of the 2nd support layer, it is controlled further that the 2nd support enters, and by the cell septum front face and the pore internal surface with big pore size, the 2nd support layer is further unevenly distributed in the front face of the 1st support layer, and is formed in it.

[0036]

Therefore, according to the manufacture approach of this invention, the shape of toothing of a catalyst bed can be formed still more certainly, and the operation effectiveness by the emission-gas-purification filter catalyst of above-mentioned this invention can be raised further.

[0037]

As for the amount of coats of the 1st support layer, in the manufacture approach of this invention, it is desirable to consider as per [ honeycomb structure object 1L / 30-150g ]. The 1st support layer is NOx at less than 30 g/L. It is NOx when occlusion material is supported. If the fall of the endurance of occlusion ability is not avoided but 30 g/L is exceeded, small pore will carry out blinding and a pressure loss will go up. Moreover, as for the amount of coats of the 2nd support layer, it is desirable to consider as per [ honeycomb structure object 1L / 30-150g ]. the effectiveness which the 2nd support layer made the shape of toothing in less than 30 g/L is not acquired -- if 150 g/L is exceeded, big pore will carry out blinding and a pressure loss will go up rapidly. Moreover, by the above-mentioned reason, it is per [ honeycomb structure object 1L ] by the sum total of the 1st support layer and the 2nd support layer. It is desirable to be referred to

as 100-200g.

[0038]

The catalyst metal contained in a catalyst bed is NO<sub>x</sub> by catalytic reaction. Although it can use if it can return and oxidation of PM is promoted, it is desirable to use a kind chosen from the noble metals of platinum groups, such as Pt, Rh, and Pd, at least or two or more sorts. As for the amount of support of noble metals, it is desirable to consider as the range of per [ 1-5g ] volume of 1l. of a honeycomb structure object. It will become a cost rise while activity is saturated, even if activity will be too low, will not be practical and will support mostly from this range, if there are few amounts of support than this.

[0039]

Moreover, what is necessary is just to support using the solution which dissolved the nitrate of noble metals etc. in the coat layer which consists of oxide powder or multiple oxide powder by the adsorption supporting method, the sinking-in supporting method, etc., in order to support noble metals. Moreover, noble metals are beforehand supported to oxide powder or multiple oxide powder, and a catalyst bed can also be formed using the catalyst powder.

[0040]

A catalyst bed is NO<sub>x</sub> chosen from the alkali metal, alkaline earth metal, and rare earth elements which were supported by either [ at least ] the 1st support or the 2nd support. It is desirable to include occlusion material. It is NO<sub>x</sub> to a catalyst bed. NO<sub>2</sub> generated by oxidation by the catalyst metal when occlusion material was included NO<sub>x</sub> Since occlusion can be carried out to occlusion material, it is NO<sub>x</sub>. Purification activity improves further. This NO<sub>x</sub> As occlusion material, it can choose from rare earth elements, such as alkaline earth metal, such as alkali metal, such as K, Na, Cs, and Li, and Ba, calcium, Mg, Sr, or Sc, Y, Pr, Nd, and can use. It is NO<sub>x</sub> especially. The thing of the alkali metal which excelled in occlusion ability, and alkaline earth metal for which a kind is used at least is desirable.

[0041]

This NO<sub>x</sub> As for the amount of support of occlusion material, it is desirable to consider as the range of 0.15-0.45 mols per volume of 1l. of a honeycomb structure object. If activity is too low and it is not practical, if there are few amounts of support than this, and it supports mostly from this range, noble metals will be covered and activity will come to fall. Moreover, NO<sub>x</sub> What is necessary is just to support using the solution which dissolved acetate, a nitrate, etc. in the coat layer which consists of the 1st support and the 2nd support by the sinking-in supporting method etc., in order to support occlusion material. Moreover, it is NO<sub>x</sub> beforehand to oxide powder or multiple oxide powder. Occlusion material is supported and a catalyst bed can also be formed using the powder.

[0042]

NO<sub>x</sub> As for occlusion material, supporting to the 2nd support at least is desirable. In the part in which the 2nd support exists, since the thickness of a catalyst bed is thick, it is NO<sub>x</sub>. The reaction of occlusion material and a cel septum can be controlled and it is NO<sub>x</sub>. The endurance of decontamination capacity improves.

[0043]

Moreover, a catalyst bed is NO<sub>x</sub> at low temperature. It adsorbs and is NO<sub>x</sub> at an elevated temperature. NO<sub>x</sub> to emit It is also desirable that adsorption material is included. In a low-temperature region, NO in exhaust gas is NO<sub>2</sub>. It carries out and is NO<sub>x</sub>. Adsorption material is adsorbed and it is NO<sub>x</sub> at a pyrosphere. Adsorption material to NO<sub>2</sub> NO<sub>2</sub> from which it was \*\*\*\*\*ed and desorbed Oxidation purification of PM is promoted. This NO<sub>x</sub> As adsorption material, the powder which supported noble metals to the zirconia, or the powder which supported noble metals to CeO<sub>2</sub> can be used.

[0044]

NO<sub>x</sub> To the downstream of adsorption material, it is NO<sub>x</sub> in a catalyst metal. It is also desirable to support occlusion material. NO generated by the reaction with PM by carrying out like this is NO<sub>x</sub> of the downstream. Occlusion is carried out to occlusion material and reduction purification is carried out. Moreover, it is NO<sub>x</sub> to the upstream. Since occlusion material is not supported, in the part, it is NO<sub>x</sub>. The reaction of occlusion material and a cel septum cannot arise, but thickness of a catalyst bed can be made thin, and increase of a pressure loss can be controlled further.

[0045]

[Example]

Hereafter, an example explains this invention concretely.

[0046]

(Example of a trial)



Diameter 129mm, die length 150mm, volume of about 2000 cc, the number of cels 300 cels / inch<sup>2</sup> The base material of a straight honeycomb configuration with a square cel was prepared. The porosity of a base material is 65% and average pore size is 23 micrometers.

[0047]

Next, the paste of the shape of a cream which mixes the organic binder and water of the specified quantity to the powder of the cordierite presentation which consists of an alumina, talc, a kaolin, and a silica, and has the stable firmness in it is prepared. Using this paste, using the paste impregnation machine (dispenser) with the pipe of predetermined die length, the weather strip of the 1 every \*\* was carried out to the upstream end face of a base material by turns, and the upper plug was formed. On the other hand, in the downstream end face of a base material, the weather strip of the cel without an upper plug was carried out, and the downstream plug was formed. It calcinated at 1400 degrees C after that, and the honeycomb structure object with an inflow side cel and an outflow side cel was formed.

[0048]

this honeycomb structure object -- using -- mean particle diameter the wash coat of the slurry which is mainly concerned with 0.5-micrometer alumina powder is carried out -- 110 degree C -- after desiccation It calcinated at 450 degrees C and the coat layer was formed. The count of this coat process was changed and two or more kinds of honeycomb structure objects with the coat layer by which the coat was carried out in the various amount of coats were produced. Two or more kinds of honeycomb structure objects which, on the other hand, have the coat layer by which the coat was similarly carried out in the various amount of coats using alumina powder with a mean particle diameter of 3 micrometers were produced.

[0049]

The exhaust air system of 2L diesel power plant is equipped with a honeycomb structure object with various coat layers, and the honeycomb structure object which does not have a coat layer as a blank, respectively, and they are 1600 rpm x 30Nm and entering gas temperature. 200-degree C exhaust gas is circulated and PM is per [ honeycomb structure object 1L ]. The pressure loss when depositing 0.5g was measured, respectively. Pressure loss when not having a coat layer for a result The relative value when being referred to as 100 shows to drawing 7 .

[0050]

Although a pressure loss will not be concerned with the particle size of alumina powder from drawing 7 if the amount of coats is about 80 or less g/L, with the big alumina powder of the diameter of a grain which becomes the amount of coats beyond it, it turns out that the pressure loss is increasing rapidly. Therefore, the amount of coats When considering as 150 g/L, it is mean particle diameter. With 0.5 micrometers powder and powder with a mean particle diameter of 3 micrometers, since it was desirable to carry out the coat of 75 every g/L, respectively, in the example 1, we decided to make it such.

[0051]

(Example 1)

The sectional view and its important section expanded sectional view of an emission-gas-purification filter catalyst of this example are shown in drawing 1 . This emission-gas-purification filter catalyst consists of a honeycomb structure object 1, and the 1st support layer 2 and the 2nd support layer 3 formed in the cel septum 12 of the honeycomb structure object 1.

[0052]

the cel septum 12 which divides the outflow side cel 11 by which the honeycomb structure object 1 adjoined the inflow side cel 10 by which the weather strip was carried out by the exhaust gas downstream, and the inflow side cel 10, and the weather strip was carried out by the exhaust gas upstream, and the inflow side cel 10 and the outflow side cel 11 -- since -- it is constituted. The small small pore 13 of a path and the big large pore 14 of a path exist in the cel septum 12 at random, and the 1st support layer 2 is mostly formed in the front face of the cel septum 12, the internal surface of the small pore 13, and the internal surface of the large pore 14 at homogeneity. On the other hand, although the 2nd support layer 3 is formed as the upper layer of the 1st support layer 2 by the front face of the cel septum 12, and the internal surface of the large pore 14, it is hardly formed in the internal surface of the small pore 13.

[0053]

Hereafter, the manufacture approach of this emission-gas-purification filter is explained, and it replaces with detailed explanation of a configuration.

[0054]

Diameter 129mm, die length 150mm, volume of about 2000 cc, the number of cels 300 cels / inch<sup>2</sup> The base material of a straight honeycomb configuration with a square cel was prepared. The porosity of a base

material is 65% and average pore size is 23 micrometers.

[0055]

Next, the paste of the shape of a cream which mixes the organic binder and water of the specified quantity to the powder of the cordierite presentation which consists of an alumina, talc, a kaolin, and a silica, and has the stable firmness in it is prepared. Using this paste, using the paste impregnation machine (dispenser) with the pipe of predetermined die length, the weather strip of the 1 every \*\* was carried out to the upstream end face of a base material by turns, and the upper plug was formed. On the other hand, in the downstream end face of a base material, the weather strip of the cel without the upper plug 15 was carried out, and the downstream plug was formed. It calcinated at 1400 degrees C after that, and the honeycomb structure object 1 with the inflow side cel 10 and the outflow side cel 11 was formed.

[0056]

then, an alumina, a titania, and a zirconia -- a principal component -- carrying out -- mean particle diameter the slurry which is mainly concerned with the 0.5-micrometer 1st support powder is made to flow in the inflow side cel 10 and the outflow side cel 11, and carries out a wash coat to the honeycomb structure object 1 -- 110 degree C -- after desiccation It calcinated at 450 degrees C and the 1st support layer 2 was formed. As for the 1st support layer 2, 75g per l. of honeycomb structure objects 1 was formed.

[0057]

subsequently, the slurry which uses an alumina, a titania, and a zirconia as a principal component, and is mainly concerned with the 2nd support powder with a mean particle diameter of 3 micrometers is made to flow in the inflow side cel 10 and the outflow side cel 11, and a wash coat is carried out to the honeycomb structure object 1 with the 1st support layer 2 -- 110 degree C -- after desiccation It calcinated at 450 degrees C and the 2nd support layer 3 was formed. As for the 2nd support layer 3, 75g per l. of honeycomb structure objects 1 was formed.

[0058]

Then, Pt, Li, Ba, and K were supported by the sinking-in supporting method, respectively. 3g and Li the amount of support per l. of the honeycomb structure object 1 0.2 mols and Ba 0.1 mols and K are 0.05 mols.

[ Pt ]

[0059]

According to the above-mentioned manufacture approach, mean particle diameter The 1st support powder of the minute particle size which is 0.5 micrometers adheres to the front face of the cel septum 12, the internal surface of the small pore 13, and the internal surface of the large pore 14 mostly at homogeneity, and the thin uniform 1st support layer 2 is formed. And if the coat of the slurry of the 2nd support powder with a mean particle diameter of 3 micrometers is carried out, since it will be hard to go into the small pore 13, it adheres to the front face of the 1st support layer 2 in the front face of the cel septum 12, and the internal surface of the large pore 14, and the 2nd support layer 3 of a convex configuration is formed.

[0060]

(Example 2)

The emission-gas-purification filter catalyst of an example 2 was prepared like the example 1 except having made the slurry flow only into the outflow side cel 11 at the time of formation of the 2nd support layer 3, and the honeycomb structure object 1 having formed the 50g per l. of the 2nd support layers 3.

[0061]

This emission-gas-purification filter catalyst is the same configuration as an example 1 except the 2nd support layer 3 not being formed in cel septum 12 front face of the inflow side cel 10, as shown in drawing 2.

[0062]

(Example 3)

the same honeycomb structure object 1 as an example 1 -- using -- an alumina, a titania, and a Pt-Pd support zirconia -- a principal component -- carrying out -- mean particle diameter the slurry which is mainly concerned with the 0.5-micrometer 1st support powder is made to flow in the inflow side cel 10 and the outflow side cel 11, and carries out a wash coat to the honeycomb structure object 1 -- 110 degree C -- after desiccation It calcinated at 450 degrees C and the 1st support layer 2 was formed. As for the 1st support layer 2, 75g per l. of honeycomb structure objects 1 was formed.

[0063]

In addition, a Pt-Pd support zirconia is NO<sub>x</sub> which supported the water solution of colloid platinum and a palladium nitrate with carrying out sinking-in support as Pt-Pd compound noble metals to zirconia powder. In the 1st support layer 2 which is adsorption material and was obtained, per [ of the honeycomb structure

object 1 / Pt and Pd ] l. are each. 1.5g is supported.

[0064]

subsequently, the slurry which uses an alumina, a titania, and a zirconia as a principal component, and is mainly concerned with the 2nd support powder with a mean particle diameter of 3 micrometers is made to flow in the outflow side cel 11 like an example 2, and a wash coat is carried out to the honeycomb structure object 1 with the 1st support layer 2 -- 110 degree C -- after desiccation It calcinated at 450 degrees C and the 2nd support layer 3 was formed. As for the 2nd support layer 3, 50g per l. of honeycomb structure objects 1 was formed.

[0065]

Then, Pt, Li, Ba, and K were supported in the 2nd support layer 3, respectively by the sinking-in supporting method make a water solution flow only in the outflow side cel 11. 3g and Li the amount of support per l. of the honeycomb structure object 1 in the 2nd support layer 3 0.2 mols and Ba 0.1 mols and K are 0.05 mols.

[ Pt ]

[0066]

(Example 1 of a comparison)

The 2nd support powder with a mean particle diameter of 3 micrometers is used at the time of formation of the 1st support layer 2, and it is mean particle diameter at the time of formation of the 2nd support layer 3. The emission-gas-purification filter catalyst of the example 1 of a comparison was prepared like the example 1 except having used the 0.5-micrometer 1st support powder.

[0067]

(Example 2 of a comparison)

It is the 1st support layer 2 per [ of the honeycomb structure object 1 ] l. The emission-gas-purification filter catalyst of the example 2 of a comparison was prepared like the example 1 except having formed 150g and having not formed the 2nd support layer 3.

[0068]

<A trial and evaluation>

The amount of entering smokes which equipped the exhaust air system of 2L diesel power plant with the emission-gas-purification filter catalyst of examples 1 and 2 and the examples 1 and 2 of a comparison, respectively, and was measured with 2450 rpmx52Nm, the Lean stationary, the entering gas temperature of 300 degrees C, and a smoke meter Exhaust gas was circulated on 6.5% of conditions, and the amount of PM uptake and pressure-drop-buildup behavior were measured. The relation between the amount of PM uptake and a pressure loss is shown in drawing 3 , and the relation between the amount of PM uptake and collection efficiency is shown in drawing 4 , respectively.

[0069]

Since near and a pressure loss are proportional to the amount of PM uptake mostly at the straight line compared with each example of a comparison, as for the curve of the catalyst of each example, drawing 3 shows that the fall of pressure-loss detection sensitivity is controlled for the direction of the catalyst of each example compared with each example of a comparison. Moreover, from drawing 4 , the catalyst of each example is understood that collection efficiency is also high compared with each example of a comparison.

[0070]

That is, according to the emission-gas-purification filter catalyst of this invention, uptake of the PM can be carried out efficiently, and moreover, when the alimentation of PM can be presumed by detecting a pressure loss since pressure-loss detection sensitivity is high and a pressure loss exceeds a reference value, PM can be burned in little alimentation by regenerating passing hot exhaust gas etc. It can prevent that the continuation playback type DPF serves as an elevated temperature by this at the time of combustion, and faults, such as an erosion, can be prevented beforehand.

[0071]

Next, the exhaust air system of 2L diesel power plant is equipped with the emission-gas-purification filter catalyst of examples 1-3 and the examples 1 and 2 of a comparison, respectively, and it is in 11 Lap mode (entering gas temperature 220 to 370 degree C). PM oxidation quotient was computed after 200km transit, respectively from the weight difference of the value of the amount of PM in amount of PM in entering gas-appearance gas, and the amount of deposition residual PM. A result is shown in drawing 5 .

[0072]

moreover, the exhaust air system of 2L diesel power plant is equipped with the emission-gas-purification filter catalyst of examples 1-3 and the examples 1 and 2 of a comparison, respectively -- after the heat durability which circulates the inside of exhaust gas of 650 degree C for 50 hours, and 2900 rpmx80Nm and

entering gas temperature NO<sub>x</sub> after adding and circulating gas oil in 300-degree C exhaust gas The amount of occlusion was measured, respectively. A result is shown in drawing 6 . In addition, it was made for the addition of gas oil to serve as 3% of rates of fuel consumption aggravation.

[0073]

It is clear for the catalyst of each example to show high PM oxidation quotient compared with each example of a comparison, and to excel drawing 5 in PM decontamination capacity. Moreover, although PM oxidation ability of an example 2 is improving from the example 1, since the 2nd support layer 3 is not formed in the inflow side cel 10, this is considered because the contact probability with the increase of the amount of PM, and caught PM and the catalyst metal which flows into the interior of the pore of the cel septum 12 increased. For an example 3, PM oxidation quotient is still higher than an example 2, and this is NO<sub>x</sub>. NO<sub>2</sub> emitted from the adsorption catalyst Since PM oxidized, it thinks.

[0074]

Furthermore in drawing 6 , the catalyst of an example 1 is NO<sub>x</sub> after durability from each example of a comparison. Since the catalyst bed of a part in which it turns out that there are many amounts of occlusion, and the 2nd support layer 3 is formed is thick, this is NO<sub>x</sub>. Since the reaction of occlusion material and the cel septum 12 was controlled, it thinks. In addition, an example 2 and an example 3 are NO<sub>x</sub>. Although occlusion ability is inferior compared with an example 1, in the examples 2 and 3, the amount of coats of the 2nd support layer 3 is considered because it is few compared with an example 1.

[0075]

On the other hand, since the coat of the 2nd support powder with a big particle size is carried out previously and the coat of the 1st support powder with a particle size small after that is carried out, the 1st support powder is filled up with the example 1 of a comparison into the clearance between the 2nd support powder, consequently it is thought in it that the shape of toothing of a catalyst bed was hardly formed. Therefore, effectiveness is not looked at by pressure-loss behavior, PM collection efficiency, etc. like the example 2 of a comparison, but it has become a property equivalent to the example 2 of a comparison.

[0076]

[Effect of the Invention]

That is, according to the emission-gas-purification filter catalyst of this invention, while PM decontamination capacity improves, the fall of pressure-loss detection sensitivity is controlled.

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view and important section expanded sectional view of an emission-gas-purification filter catalyst of this invention. [ of one example ]

[Drawing 2] It is the important section expanded sectional view of the emission-gas-purification filter catalyst of the 2nd example of this invention.

[Drawing 3] It is the graph which shows the relation of the pressure loss to the amount of PM uptake.

[Drawing 4] It is the graph which shows the relation of PM collection efficiency over the amount of PM uptake.

[Drawing 5] It is the graph which shows PM oxidation quotient of the catalyst of an example and the example of a comparison.

[Drawing 6] NO<sub>x</sub> after the durability of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.

[Drawing 7] It is the graph which shows the amount of coats, and the relation of a pressure loss.

[Description of Notations]

1: Honeycomb structure object 2: The 1st support layer 3: The 2nd support layer

10: Inflow side cel 11: Outflow side cel 12: Cel septum

13: Small pore 14: Large pore

---

[Translation done.]

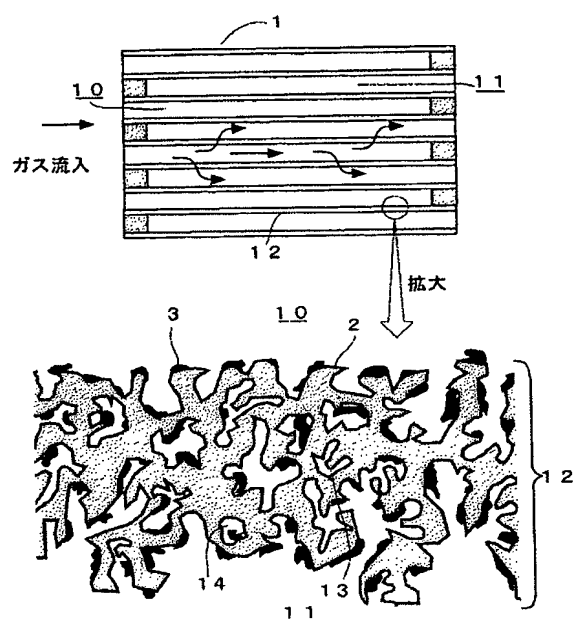
## \* NOTICES \*

JPO and NCIP are not responsible for any damages caused by the use of this translation.

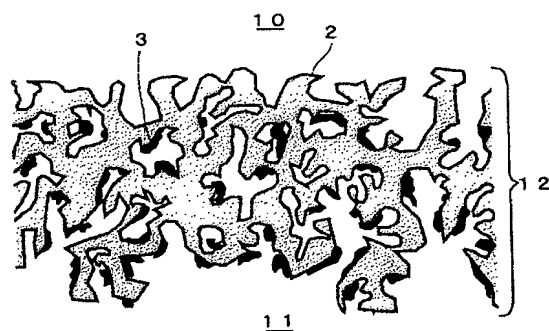
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

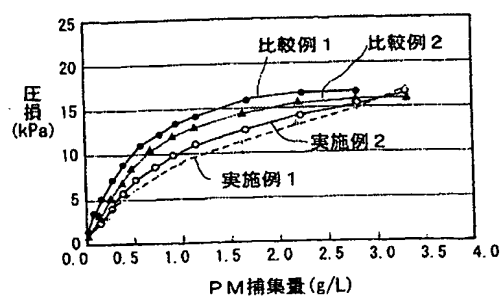
[Drawing 1]



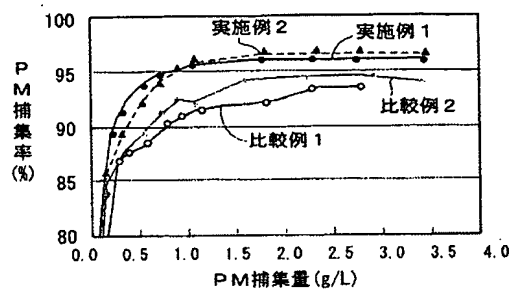
[Drawing 2]



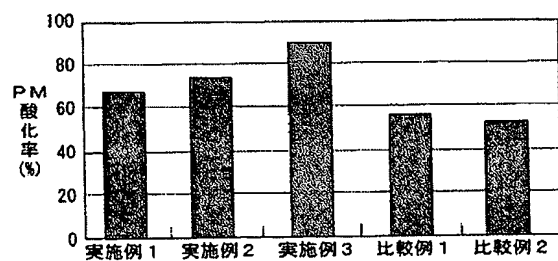
[Drawing 3]



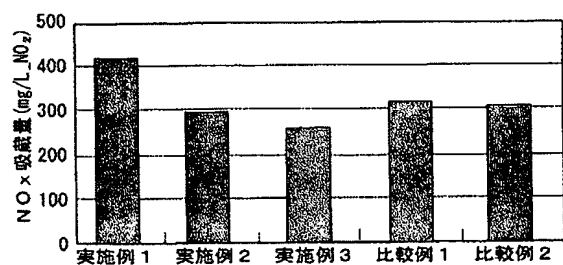
[Drawing 4]



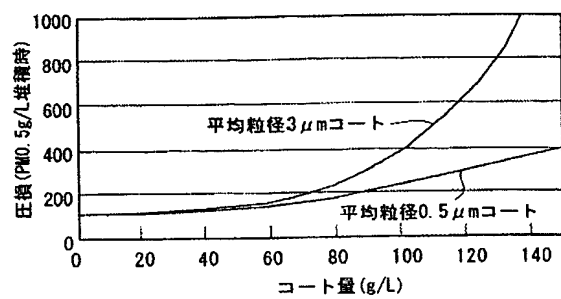
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]